PTO 2006-3363

Japanese Kokai Patent Publication No. S55-5938, published January 17, 1980;

Application No. S53-77881, filed June 27, 1978; Inventor: Masaru SUZUKI, Yuzo SHIMIZU, and Tomoyuki MINAMI

Assignee: Toray Ind Inc

WATER-SOLUBLE POLYESTER ADHESIVE

---

1. Title of Invention:

Water-Soluble Polyester Adhesive

2. Claims

In a polyester copolymer made up of dicarboxylic acid, consisting of aromatic dicarboxylic acid component and fatty acid component in a molar ration between 10/1 and 1/10 and/or its ester-producing derivative, and a glycol,

a water-soluble polyester adhesive made with a composition ratio of

A ester-producing sulfonic acid alkaline metal salt compound making up 3~10 mol% of the entire acidic component, and

B 1, 4-bis (hydroxy-alkoxy) benzene component making up 5~60 mol% of the glycol component.

3. Detailed Explanation of Invention

This invention concerns a water-soluble adhesive of polyester origin, more specifically, it concerns a water-soluble polyester adhesive with superior adhesion to gelatin, polyvinyl alcohol etc. and improved operational environment. Since straight-chain polyester film, and in particular, polyethylene terephthalate biaxially stretching films, have excellent transparency, size stability, toughness, these properties have been widely used in Prior Art in photographic sensitive material, in bases for metal vapor deposition, bases for drafting, bases for magnetic tapes, wrapping material etc. In this case it is very rare for a polyester film to be used by itself, for example, when it is used as photographic film base. For example, in the event of a photographic film adhesion between layers of gelatin must be imparted, in the case of a magnetic tape base, adhesion to the magnetic layer must be imparted, in the event of bases for drafting, adhesion to a matting agent layer must be imparted.

However, generally speaking there is drawback in that adhesives that possess affinity to polyester film surfaces, have poor adhesion to the surface layer agent, or if they possess affinity to the surface layer agent, they have poor adhesion to the polyester film surface.

On the other hand, in Prior Art, a lot of adhesive agents were used that are soluble in organic solvents to increase the adhesion of linear polyesters to metal foil, various

plastics, in particular, gelatin, polyvinyl alcohol, etc., but lately their use has been limited out of concern for operational environment.

In order to improve the situation on the above-mentioned issues, this invention offers polyester adhesives that are water-soluble and have superior adhesive properties. Polyesters with adhesive properties known in Prior Art include

1 the product of copolymerization of polyester with 40-80 weight% of polyalkylene ether (US Patent 3,023,192)

2 the product of copolymerization of polyethylene terephthalate with isophthalic acid, tetrahydroterephthalic acid, and fatty dicarboxylic acid, etc. (US Patetn 2,829,747, British Patent 861, 835)

3 the product of copolymerization of polyester with at least 20 mol% polyethylene glycol with a degree of polymerization from 2 to 10 and approximately 8 mol% or more of a metal salt compound of sulfonic acid (Patent of Japan S47-40873 etc.)

4 the product of copolymerization of polyester with fatty dicarboxylic acid and diethylene glycol (Patent of Japan S51-48197)

However, while both the above-mentioned polyester elastic bodies 1, 2, 4 and the adhesive agents are soluble in organic solvents, they are completely insoluble in water. Therefore when used as adhesive agents they have to be of the hot melt type and organic solvent-soluble type, which means that this is problematic for operational environment.

On the other hand, 3 concerns a polyester that possesses adhesive properties while being water-soluble, but its drawback is its extremely poor water resistance.

The authors of this invention focused their attention on a water-soluble polyester adhesive that would overcome the drawback of the known adhesives of polyester origin and resolve operational issues, and as, a result, they made this invention.

That is, this invention, in a polyester copolymer made up of dicarboxylic acid, consisting of aromatic dicarboxylic acid component and fatty acid component in a molar ration between 10/1 and 1/10 and/or its ester-producing derivative, and a glycol,

is a water-soluble polyester adhesive made with a composition ratio of

A ester-producing sulfonic acid alkaline metal salt compound making up 3~10 mol% of the entire acidic component, and

B 1, 4-bis (hydroxy-alkoxy) benzene component making up 5~60 mol% of the glycol component.

The aromatic dicarboxylic acid components used in this invention include terephthalic acid,isophthalic acid, phthalic acid, 2,5-dimethylterephthalic acid, 2,6-naphthalene dicarboxylic acid, 1,4-napthalene dicarboxylic acid, 2,5-naphthalene dicarboxylic acid, biphenyl dicarboxylic acid, and their ester-producing derivatives; in particular, especially desirable results with regard to spreadability on a polyester substrate and solubility in water are achieved by using terephthalic acid (or its ester-producing derivatives) along with isophthalic acid (or its ester-producing derivatives).

The fatty acids used include adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid and at least one of their ester-producing derivatives.

Moreover, the mol ratio of aromatic dicarboxylic acid component and fatty dicarboxylic acid component as parts of the total acid component is within the range of 10/1~1/10, and yields superior effect in terms of adhesiveness to polyester substrate and gelatin, as well as resins of polyolefinic or polyvinyl alcohol origin. If this mol ratio is lower than 0.1 fatty dicarboxylic acid component per 1 aromatic dicarboxylic acid component, water solubility, uniform spreadability, and adhesiveness are all insufficient; if on the other hand, it exceeds 10, water resistance becomes a problem, which makes this undesirable.

Copolymerization of the above-mentioned structure with ester-producing sulfonic acid alkaline metal salt compound can promote solubility in water and increase the adhesive effect.

These ester-producing sulfonic acid alkaline metal salt compounds include alkaline metal salts of sulfoterephthalic acid, 5-sulfoisophthalic acid, 4-sulfoisophthalic acid, 4-sulfonaphthalene-2,7-dicarboxylic acid, sulfo-p-xylyleneglycol-2-sulfo1,4-bis (hydroxyethoxy) benzene, etc., as well as their ester-producing derivatives, preferably, sodium and potassium salts of 5-sulfoisophthalic acid, and sulfoterephthalic acid.

However, in the event that the metal salts of sulfonate compounds are those of non-alkaline metals, the water solubility of the resulting polymers is low, and it is impossible to achieve the goal of this invention.

The above-mentioned effect can be manifested by keeping the added amount of ester-producing sulfonic acid alkaline metal salt compounds at 3~10 mol% of the total acid component.

With amounts under 3 mol% the solubility of the resulting polymers in water and their stability as water solutions drop dramatically, while upwards of 10 mol%, water resistance of the adhesive layer at the stage of usage is poor, which is undesirable. The 1, 4-bis(hydroxyalcoxy) benzene used in this invention imparts appropriate elasticity at normal temperature and increases adhesion; in addition, it can promote an auxiliary effect conducive to water solubility; the maximum effect is manifested if its amount is at 5 mol% ~ 60 mol% of the metal glycol component, preferably, 20 ~ 50 mol%.

It is undesirable that the amount be under 5 mol% because of the deterioration of impact peeling force. Nor is it desirable that it be more than 60 mol% because of poor water resistance.

Apart from 1, 4-bis(hydroxyalcoxy) benzene component, glycol components to be used jointly include ethylene glycol, 1, 2-propanediol, 1, 3-propanediol, 1,4-butanediol, 1, 5 – pentanediol, 1, 5 – pentanediol, 1, 6 –hexanediol, neopentyl glycol, 1, 8-octanediol, 1, 3-cyclohexane dimethanol, 1, 2 – cyclohexane dimethanol, 1, 4 – cyclohexane dimethanol, etc, but particularly desirable are ethylene glycol, 1, 3 – propanediol, 1, 4 – butanediol, etc.

Specific 1, 4 – bis (hydroxyalcoxy) benzenes include 1, 4 – bis (hydroxyethoxy) benzene, 1, 4 – bis (hydroxypropoxy) benzene, 1, 4 – bis (hydroxybutoxy) benzene, etc.

In the synthesis of the polyester copolymer, which is the adhesive agent of this invention, the same methods can be used as are applied in the preparation of polyethylene terephthalate.

For example, method 1: the predetermined amounts of dimethyl ester of dicarboxylic acid and glycol, calcium 1-hydroacetate, manganese-4-hydroacetate, magnesium-4 hydroacetate, zinc-2-hydroacetate, etc. in the presence of conventional ester exchange catalysts were heated to 140 ~ 240°C, and while the resulting methanol was being distilled, the ester exchange reaction was conducted. Next, 1, 4-bis (hydroxyalcoxy) benzene component and a polymerization catalyst of which representative are antimony trioxide, germanium dioxide, tetrabutyl titanate, etc, and in the presence of phosphorus compounds, such as phosphorous acid, phosphoric acid (and/or their ester compounds), underwent polycondensation as the glycol was distilled at a high temperature and vacuum of 200 ~ 290 °C and 0.01~ 50 mm Hg, where 1, 4-bis(hydroxyalcoxy)benzene was added prior to ester exchange. Method 2: dicarboxylic acid and glycol are esterified while distilling water that is generated at 150~250°C at normal or increased pressure, and then undergoes polycondensation in the presence of 1, 4 – bis(hydroxyalcoxy) benzene component, a phosphorus compound, and a polycondesation catalyst.

If the ester-producing sulfonic acid alkaline metal salt compound is an ethylene glycol ester of a carboxylic acid or oxycompound, it is preferably added after the ester exchange or the esterification, but if it is a dimethyl ester of a dicarboxylic acid, then it is preferably added prior to the ester exchange; also, if it is a dicarboxilic acid, it is preferably added prior to esterification.

When the aromatic dicarboxylic acid component is a dialkyl ester while the fatty dicarboxylic acid component is a fatty dicarboxylic acid, polycondensation can be completed with the former undergoing common ester exchange and then the latter undergoing esterification.

To increase the heat resistance of the copolymerized polyester, hindered phenols and other antioxidants can be added; to increase the sliding properties, inorganic microparticles or organic lubricants can be added as well as pigments, dyes, or water-soluble or moisture-dispersing polymers other than the copolymerized polyester in question.

The copolymerized polyester adhesive of this invention is used as a water solution, but this is not a water solution in the strict physical and chemical sense: while a large part is dissolved, part of it is included as microdispersion.

Compared to the polyester adhesive of Prior Art, the water-soluble copolymerized polyester adhesive of this invention has the following characteristic features.

a. Since it does not use organic solvents considerations with regard to toxicity, flammability, and other operational environment issues have become much more straightforward.

b. Since it is a water-soluble type, it can be used in a wide range of applications where the hot melt type cannot be used; it can be especially effectively used as s sizing agent in weaving, and as a fiber and film coating agent.

c. It can be effectively used also in thermal adhesive applications, for example a water solution of the adhesive agent of this invention may be applied to a substrate and the, once the water evaporates, an adhesive film of the said copolymerized polyester can be formed on the substrate, which can be followed by pressure or thermal adhesion.

d. In particular, it possesses a superior adhesive effect for polyester film and polyvinyl alcohols, gelatin, and polyolefins.

Below, we will explain this invention in detail citing Experiments and Comparison Experiments

The resulting copolymerized polyester was tested using the following evaluation methods

(1) Water solubility

50 g of the above-mentioned copolymerized polyester that was melted at 210 °C in a nitrogen atmosphere was poured into 1 l of hot water at 95°C and dissolved. The solution container was equipped with a mixing device and a reflux device and the solution continued for 40 minutes with gentle agitation.

Next, this water solution was gradually cooled to room temperature, and its appearance was judged.

(2) Adhesion properties with regard to polyvinyl alcohol

A 50 μ-thick biaxially stretching film of polyethylene terephthalate was coated with the said water solution and dried in a stretched position for 2 minutes at 180°C, whereupon to this adhesive surface was applied a 4% water solution of polyvinyl alcohol with a 99% degree of saponification, which was followed by drying for 3 minutes at 120 °C

The resulting laminated film was left to sit for 24 hours in 65% RH atmosphere at 40°C for a period of 1 month and then 24-mm wide adhesive tape manufactured by Nichiban was glued to the polyvinyl alcohol surface and peeled off along the 180° direction, with the adhesive strength being demonstrated in 5 grades

1: the adhesive strength is very weak; the adhesive tape is peeled off completely

2: over 50% is peeled off with cellotape

3: 10~50% is peeled off with cellotape

4: the adhesive strength is quite strong, no more than 10% is peeled off

5: the adhesive strength is exrtremely strong, no peeling off at all.

(3) Adhesion properties with regard to gelatin

based on item (2)

(4) Water resistance

A 50 μ-thick biaxially stretching film of polyethylene terephthalate was coated with the said water solution and dried in a stretched position for 2 minutes at 180°C; then using an electric iron at 140° enmeshing through the coating surface was performed.

This film was treated in hot water at 85°C for 30 minutes, and the strength was displayed in 5 grades using the comparison of strength before and after the hot water treatment.

1: The strength was 50% of that of the object not treated with hot water.

2: ' about 70~50% "

3: ' 90~70% "

4: ' 95~90% "

5: ' over 95% "

(5) Uniform coating properties

These were displayed by the state of a biaxially stretching film of polyethylene terephthalate to which said water solution was applied with a gravure roll.

Experiment 1

36.9 parts by weight dimethyl terephthalate, 30.4 parts by weight dimethyl isophthalate, 9.8 parts by weightdimethyl-5-sodium sulfoizophthalate ester, 51.8 parts by weight ethylene glycol, 37.7 parts by weight 1,4-bis(hydroxyethoxy) benzene, and 0.069 parts by weight calcium acetate were mixed together and subjected to ester exchange reaction in a flow of nitrogen at 140°C - 220°C, while methanol was being distilled. Then 0.05 parts by weigh trimethyl phosphate, 0.04 parts by weight antimony trioxide as the polymerization catalyst, and 13.9 parts by weight adipic acid were added and underwent esterification at a reaction temperature of 220 – 230 °C, with almost the theoretical amount of water distilled.

Next, pressure was reduced and temperature increased in the system until ultimately polymerization went on for 4 hours at 285°C and 0.2 mm Hg.

The limiting viscosity of the resulting polyester copolymer was 0.69.

50 g of the said polyester copolymer were dissolved for 30 minutes in hot water at 95°C yielding a somewhat white and turbid 5% water solution.

On the other hand, a 50 μ-thick biaxially stretching film of polyethylene terephthalate was coated with the resulting water solution of the polyester copolymer and dried for 2 minutes while being stretched at 180°C, whereupon to this coated surface was applied a 4% water solution of polyvinyl alcohol with a 99% degree of saponification, which was followed by drying for 3 minutes at 120 °C.

A sticky tape was applied to the polyvinyl alcohol surface of the resulting laminated film, and, in the case of peeling off along the direction 180°, when its peel-off strength was studied, it was clear that it had an extremely high adhesion strength, with no peel-off between any of the layers. Table 1 shows composition comparison and evaluation. (Experiment 1)

Below, the polycondensation reaction was conducted by the same method except with varying kinds and mol ratios of aromatic dicarboxylic acids and fatty dicarboxylic acids, varying amounts of dimethyl-5-sodium sulfoisophthalate and of 1,4-bis(hydroxyethoxy)